(12) UK Patent Application (19) GB (11) 2 120 228 A

(21) Application No **8236194**
(22) Date of filing **20 Dec 1982**
(30) Priority data
(31) **289381**
(32) **12 May 1982**
(33) **Argentina (AR)**
(43) Application published
30 Nov 1983
(51) **INT CL³**
C06B 47/00 31/00
(52) Domestic classification
C1D 6A1A1 6A1AY 6A1B 6A1F 6A1G 6A1H 6A2B 6BX
(56) Documents cited
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EP A 0004160
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(58) Field of search
C1D
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(54) Composition and process for the production of emulsion explosives

(57) An emulsion explosive including, an aqueous solution of inorganic oxidizing salts, a fuel reducting oil phase, and a series of emulsifiers and modifying agents of the crystalline habitat and sensitized by chemical procedures.

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SPECIFICATION

Composition and process for the production of emulsion explosives

This invention refers to a new type of emulsion explosives composition and to the method for industrial production.

It is well known that the emulsion explosives are based on the dispersion of one liquid phase, within other phase, non miscibles one into other.

This emulsion may also contain solid compounds dispersed within it. It is intended to achieve an intimate contact between an oxidizing agent, a reducting fuel, a sensitizing agent and others additives which provide to it the desired properties.

Normally the liquid phases included in this compositions are: an aqueous phase that contains inorganic oxidizing salts and an oil phase which contains the fuel; the aqueous phase is dispersed within the oil phase, producing an inversed type emulsion: water in oil.

This invention brings up some novelties to the state of the art, such as the sensitizing by a system which generates nitrogen bubbles finely dispersed within the matrix emulsion and the production of a emulsion explosives type that can be pumped or cartridged according to the relative proportion of the inorganic oxidizing salts.

If it is also considered a novelty in the present invention the use of oxigenated oils (for example: vegetable or animal fats, epoxidized oils, etc.) as basic components of the continuous dispersant phase alone or associated with other non oxigenated mineral oils, such as gas-oil. The properties of water proofing, consistency, plasticity, etc., of the emulsions are improved using adequate mixtures of emulsifiers.

The addition of products which are compatible with the system such as starch gums, aluminium powder and others, increases the stability of the emulsions and prevents the possible formation and growth of cristals from the present salts.

Concerning to the manufacturing procedure of this emulsion explosives, the present invention also brings out two advantages: the use of a continuous system of emulsification homogeneization, with special design and in certain cases the possibility of working at temperatures near the ambient.

Description of the invention

The oxidizing phase is composed by a solution of salts, generally in an aqueous medium. That is to say, it is a solution of oxidizing anions (nitrates, chlorates, perchlorates and similar others) and metal cations (Na^+, K^+, Ca^{+2}, Al^{+3}, etc.) or ammonium (NH_4^+).

Due to its special characteristics, the ammonium nitrate (AN) uses to be a main component frequently associates with sodium nitrate (SN) and/or with calcium nitrate (CN). The mixtures of (AN) with (SN) or (AN) with (CN), with the possible presence of other salts, give different properties to the emulsions that contain them, according to the percentages in which they are mixed.

For example the emulsions with sodium nitrate are usually characterized as "hard ones" due to its rheological properties and for this reason are suitable for being cartridged.

On the other hand, the rheological properties of the emulsions with calcium nitrate show viscosity values and pseudoplasticity properties that makes them specially suitable for straight pumping to the blastholes.

The water content of the oxidizing aqueous phases ranges from 10 to 20% and preferably around 15%.

The binary system AN-CN in aqueous saturated solution is specially interesting by its physicochemical properties.

For example a solution of 70 gr. ammonium nitrate in 15 gr. of water is saturated at 77°C, whereas a solution of 35 gr. AN and 35 gr CN in 15 gr of water is saturated and cristallizes at 7°C.

These facts bring out some advantages, not only for the emulsion qualities, but also for the improvement of the manufacturing procedure. Consequently, if operating with a AN/CN weight ratio comprised usually (but not exclusively) between 30/60 and 60/30, and preferably about 50/50, pumpeable explosive emulsions can be obtained having such low freezing points, that its stability is fully assured, even at temperatures substantially lower than the ambient.

Relating to its manufacturing procedure it is only necessary to heat the aqueous phase up to a relatively low temperature to solve the salts.

In some cases this fact may allow the manufacturing to be made at ambient temperature.

For the cartridgeable compositions it is more adequate to use ammonium nitrate alone or in combination with sodium nitrate in aqueous phase. A ratio of AN/SN = 75/25 to 80/20 is preferred.

The addition of sensiting agents allows an improvement of the qualities and explosive characteristics of the emulsions.

The sensitizing procedures that are followed in the present invention consist of the generation, by chemical means, of inert gas bubbles evenly distributed within the emulsion. Among the various chemical processes that can be used, it has been chosen the reaction of sodium nitrite with ammonium nitrate, in the presence of thiourea which acts as a catalyst, and some times ferric nitrate acting as a speeding up agent.

These components take part in the reaction, in ratios ranging from 0.1% to 0.7% for the thiourea, 0.1% to 10% for the sodium nitrite and 0.05% to 0.3% for the ferric nitrite, all referred to the total weight of the composition and having always an excess of ammonium nitrate present in the oxidizing phase. The final

density of the emulsion obtained following this procedure ranges between 1.5 and 0.9 grammes per cm^3.

It is necessary to disperse a big volume of aqueous phase within a relatively small volume of oil phase, to achieve an oxygen global balance close to zero in the explosive emulsions.

The volume ratio of aqueous to oil phase, can be higher than 90/10. This fact gives way to some limitations in the emulsions properties (stability, water proofing, rheology, etc.) and can difficult its manufacturing.

The oils normally used as constituents of the dispersant phase are mixtures of petroleum hidrocarbons such as gas oil, etc. with water. It is an specific purpose of the present invention to include other organic chemical materials, such as mineral, vegetal or animal oils having a certain percentage of oxygen in its molecule, as components of the dispersant of the emulsion explosives.

In this way, the volume of the oil phase can be increased in relation to the volume of the aqueous phase, or the volume of the latter can be decreased in relation to the former because a lesser quantity of a saturated solution of oxidizing salts is required to achieve an oxygen balance (O.B.) with a specific quantity of oxygenated oil, than with the same quantity of a less oxygenated oil, or an oil containing no oxygen at all.

As an example, a soy-bean oil with a content of 11% oxygen has an oxygen balance of −2,880 while an epoxydated soy bean oil with a 16.8% oxygen has an O.B. of −2,609. Both soy-bean oils are miscible between them and with gas oil. This fact allows the formulation of many different compositions of emulsion explosives.

The soy-bean oil is a triglyceride, i.e., it has the molecule of the glycerine sterified with non saturated long chained fat oils. The esthers (R-COOR) radicals, already supply oxygen to the oil molecule, but the epoxidation of the non saturated links, originates an epoxidated oil, having a higher oxygen content. This example is not limited, and obviously oils with other oxygenated radicals can be used within the innovation scheme offered by the present invention, which wide considerably the range of explosive emulsions. The optimum oxygen content of the dispersant organic phase can be achieved in each case, mixing the oxygenated and not oxygenated oils in the adequate ratio, as has been shown above.

The relative increase of the oil, hidrophobous, dispersant phase volume, implies a parallel increase of the explosive emulsion proofing to the water which is a highly desirable property. On the other hand the relative decrease of the oxidizing salts quantity, allows a relatively decrease of the aqueous phase volume, or else a decrease of the concentration of the salts which diminishes greatly the risk of a crystallization.

The stability duration and water proofing of the explosive emulsions, is strongly dependent on the use of emulsifiers being compatible with the physicochemical nature of the phases in contact. The oxygen content and the nature of the oxygenated radicals contained in the organic phase molecule fix up, at a great extent, the properties (lipopholic/hydrophilic balance, molecular structure, cathionic or anionic character, etc.) required by the surfacting agents that, placed on the interfaces, will act as emulsifiers.

The concentration of these agents, also depends on the above-mentioned factors. As a rule, this concentration will range between 0.5 to 3.0% by weight, and will be more frequently around 1.5% by weight relative to the whole composition.

The chemical nature of the emulsifiers is very varied. Usually they are chosen among compounds obtained from alkylamonium radicals, with a certain degree of nonsaturation in its alkylic chain, having chain lengths between 16 and 20 carbon atoms, or else among compounds obtained from fatty oils, such as polyalcohols (sorbitol, glycerine etc.). Specific examples are: the alkylammonium esters (acetates, etc.), the oleates, estereates, palmitates, etc. of sorbitol glycerol and many others. Frequently the rheological qualities (plasticity, flowing, etc.) of the emulsions are fixed up at a great degree by the nonsaturation degree. This nonsaturation degree can be varied by the association of more or less unsaturated emulsifiers.

Example I

a) An aqueous solution containing 42.70% of ammonium nitrate (A.N.), 45.4% of calcium nitrate (C.N.), 11.30% of water and 0.5% of thyourea is prepared. This solution crystallizes at 25°C and consequently is prepared at a soft temperature and is kept at ambient temperature.

b) A mixture of 60% of epoxidized soy-bean oil, 10% of gas oil and 30% of SPAN80, an emulsifying agent, is prepared separately to a) at a temperature of 50°C until is totally homogeneous.

c) Both solutions are mixed together in a homogeneizer, with a ratio of 92.81% of solution a) and 7.19% of solution b) and subjected to a strong agitation. At the same time that both solutions are mixed together a 0.4% of sodium nitrite must be added. The percentage is by weight relative to the total quantity of explosive to be produced.

The emulsion is instantaneously formed and is refined afterwards, passing through a colloidal mill and following the addition of solid products.

The emulsion obtained by the described discontinuous process can also be obtained by the continuous process specified in the present invention. In this process, the solution prepared according to a) and the organic mixture prepared according to b) are fed simultaneously with the sodium nitrite in a continuous flow to a specially designed emulsifier-homogeneizer system.

Example II

a) An aqueous solution containing 72.6% of A.N., 14.54% of S.N. (sodium nitrate), 0.5% of thyourea and 16.36% of water is prepared. As this solution crystallizes at 70° its preparation is made above this temperature.

b) A mixture containing 31.8% of mixed emulsifiers and 68.2% of gas oil is prepared separately to a) at a temperature comprised between 40-50°C to achieve a full homogeneization.

c) These two solutions are mixed together in a ratio of 92.39% of solution a) and 7.61% of solution b) and put in a homogeneizer under strong agitation.

At the same time that both solutions are mixed together a 0.5% of sodium nitrite must be added. This percentage is by weight and relative to the whole quantity of explosive to be produced.

The emulsion is formed up instantaneously and afterwards is processes as in Example I, although in this case the resulting emulsion is of a cartridgeable type.

Example III

a) An aqueous solution containing 83.23% of AN, 16.17% of water and 0.5% of thyourea. This solution crystallizes around 70°C, so it will be prepared above this temperature.

b) A mixture containing 26.74% of various mixed emulsifiers and 73.26% of gas oil C, is prepared separately to a), at temperature comprised between 40-50°C to achieve a full homogeneization.

c) Both solutions are mixed together in a ratio of 94.54% of solution a) and 5.46% of solution b) and put in a homogeneizer under strong agitation.

At the same time that both solutions are mixed, a 0.6% of sodium nitrite is added. This percentage is expressed by weight and relative to the whole quantity of explosive to be produced.

The next step is similar to the Examples I and II and in this case an emulsion of the cartridgeable type is produced.

Example IV

a) An aqueous solution containing 48.36% of AN, 38.16% of CN, 13.04% of water and 0.5% of thyourea is prepared. This solution crystallizes around 26°C, so it must be prepared at a soft temperature and kept at ambient temperature.

b) A mixture containing 29.24% of adequate emulsifier and 70.75% of epoxidated soybean oil is prepared separately to a) and at a temperture range of 60-70°C until a full homogeneization is achieved.

c) Both solutions are mixed together in a ratio of 90.22% and 9.78% respectively, under strong agitation, in a homogeneizer. A 0.4% by weight of sodium nitrite, referred to the whole quantity of explosive produced, is added when mixing together both solutions. The next step is similar to those in the former Examples, and the emulsion produced is of the pumpeable type.

TABLE I

	Examples			
Composition %	*I*	*II*	*III*	*IV*
A.N.	39.60	67.00	78.14	43.47
S.N.	-	13.20	-	-
C.N.	42.27	-	-	34.20
Water	10.44	11.19	15.30	11.65
Emulsifier	2.04	2.42	1.46	2.86
Gas oil	0.68	5.19	4.00	-
Epoxydated Soybean oil	4.07	-	-	6.92
Thyourea	0.5	0.5	0.5	0.5
Sodium Nitrite	0.4	0.5	0.6	0.4
Density (gr/c.c)	1.20	1.17	1.15	1.19
Rheological Characte-ristics	Pump.	Cartrgd.	Cartrgd.	Pump.
Commercial detonating velocity				
32 mm Ø	3000	2777	3559	3215
50 mm Ø	4150	4183	4311	4045
85 mm Ø	5705	4700	6122	5130
Confined detonating velocity Fe				
32 mm Ø	4892	4133	5775	4915
50 mm Ø	5188	4890	6001	5300
Power %	68	69	69.5	67.5
Hess mm.	12	11.5	12	12.5

CLAIMS

1. A new composition of emulsion explosives, featuring as main components the following: an aqueous solution of inorganic oxidizing salts; a fuel reducting oil phase, and a series of emulsifiers and modifying agents of the crystalline habitat and sensitized by chemical procedures.

2. A composition in accordance with claim 1, wherein the ratio of inorganic salts present in the aqueous phase allows to obtain pumpeable or cartridgeable emulsions. In the case of cartridgeable emulsions, the ratio by weight of AN/SN ranges from 75/25 to 80/20. In the case of pumpeable emulsions, the ratio by weight of AN/CN ranges from 30/60, and preferably 50/50.

3. A composition in accordance with claims 1 and 2, wherein the oil phase is composed of mineral vegetal or animal oils, containing a certain percentage of oxygen in their molecules.

4. A composition in accordance with claim 3, wherein the oxygenated oils used are specifically: soybean

oil and epoxidated soybean oil, separately or in their mixtures with has oil C, adjusting these mixtures to achieve the most adequate oxygen balance.

5. A composition in accordance with claims 1 to 4, wherein the emulsifier is used in a rate from 0.5% to 3% by weight and preferably the 1.5% relating to the total weight of the composition.

6. A composition in accordance with claim 5 wherein a mixture of several emulsifiers is used which contains unsaturated bonds, C-C, in its molecule, adjusting this unsaturation grade by means of the adequate rate of those in the mixture.

7. Continuous manufacturing process of the composition, in accordance with claims 1 to 6, with the aqueous phase being prepared at temperatures close to ambient, when using certain inorganic salts such as AN/CN.

8. Continuous manufacturing process in accordance with claim 7, which allows to join together the two basic operations: emulsifying the non-miscibles liquid phases, and homogeneizing the dispersed drops; both needed to obtain the desired emulsion.

9. Manufacturing process in accordance with claims 7 and 8, in which the composition is sensitized through the generation of inert gas bubbles evenly distributed within the emulsion, which are produced by the reaction of sodium nitrite with ammonium nitrate in the presence of thyourea as a catalyst and in some cases of ferric nitrate as a speeding up agent.

Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon, Surrey, 1983.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.